Understanding the stability of positive electrode materials for aqueous organic redox flow batteries

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Session Topic : Flow Batteries

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Goals and Objectives

Overall Goal

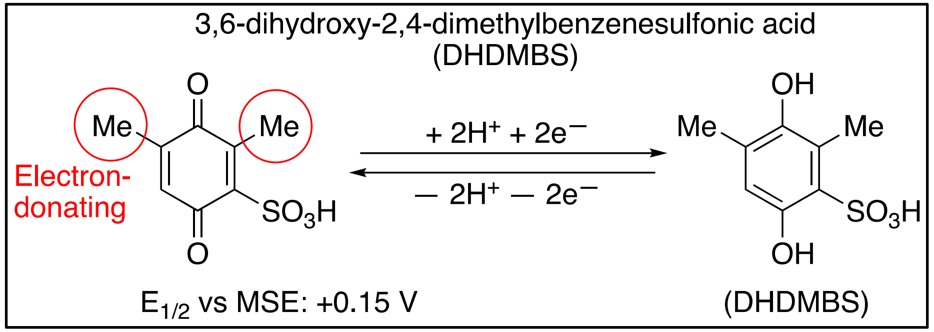
Advance the understanding of an All-Organic Water-based RFBs for cost-effective large-scale energy storage.

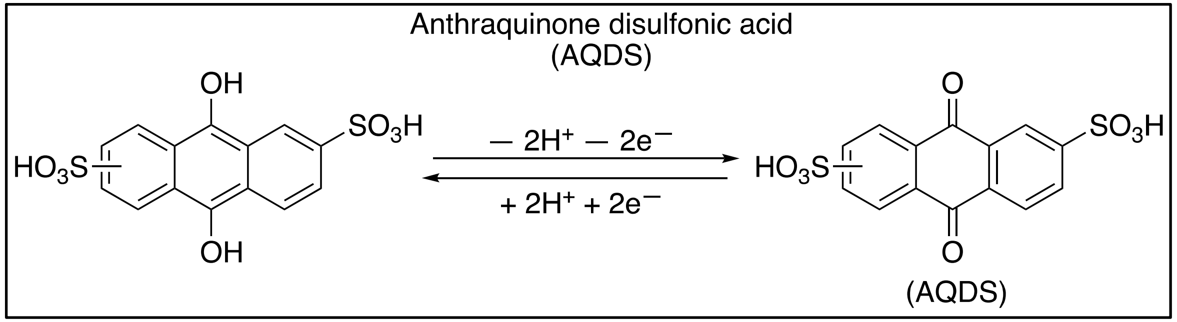
Specific Objectives

- Understand the mechanisms of degradation to formulate design rules for new molecules
- Design and demonstrate inexpensive positive side organic molecules that can be cycled repeatedly without degradation

Advances Made at USC in RFBs

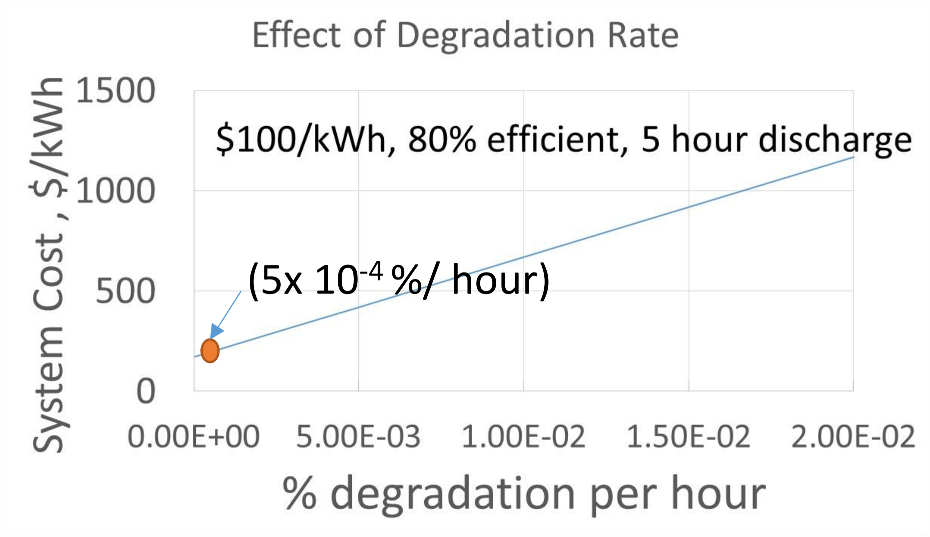
- First ever aqueous all-organic redox flow batteries based on quinone derivatives (BQDS/AQDS) in acidic media.
- Mitigated crossover by molecular design and symmetrical cycling.
- Demonstrated cycling of Michael-Reaction resistant positive side materials (DHDMBS)
- Scale up and demonstration (ITN) of 1kW/2KWh all-organic redox flow batteries (DHDMBS/AQDS) 4000 Ah/ 4.5 h per cycle with <0.01% loss/hour.
- Developed Iron sulfate/AQDS system for stable cycling over 1000 cycles with < 8 x10^{-6} %/hour.





Capacity Degradation Modes and Rates

- For realizing LCOS of < 5 cents/kWh degradation rates must be < 5×10^{-4} %/hour (<500 ppm %/hour)
- Capacity loss in water-based organic systems arises from two major processes:
  1. Chemical transformations
  2. Molecular crossover



Michael Reaction (1,4-addition) with a nucleophile such as *water, hydroxide ion or phenoxide ion.*

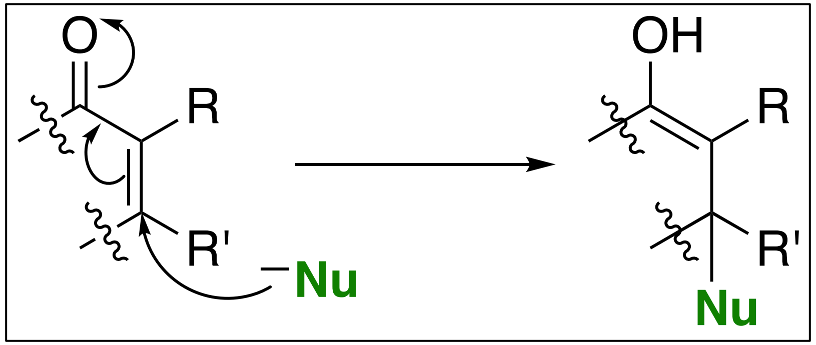
- Loss of capacity
- Decrease of cell voltage

Desulfonation or loss of the sulfonic acid group

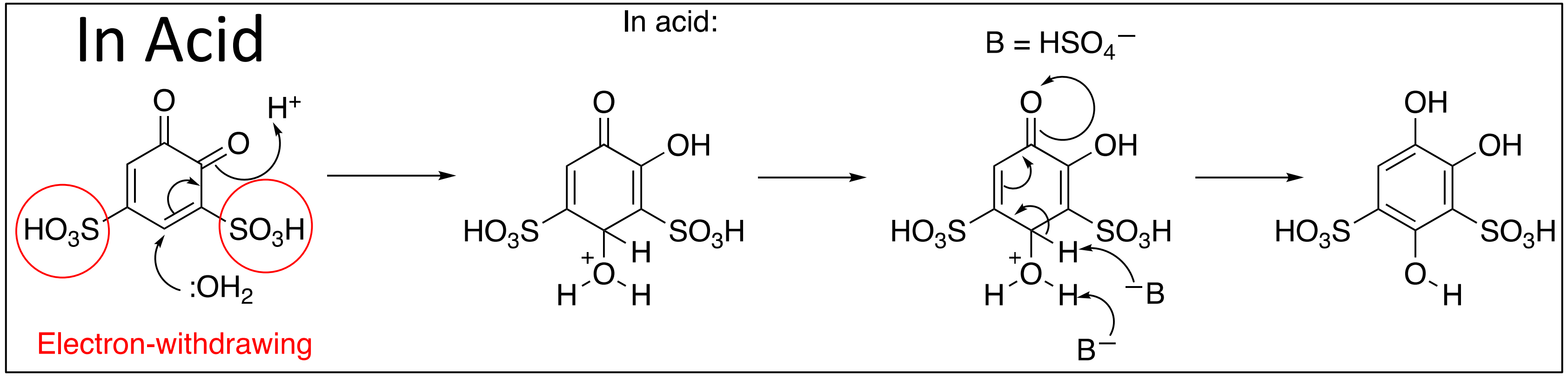
- Loss of solubility
- Decrease of cell voltage

Michael Reaction or 1,4-Addition

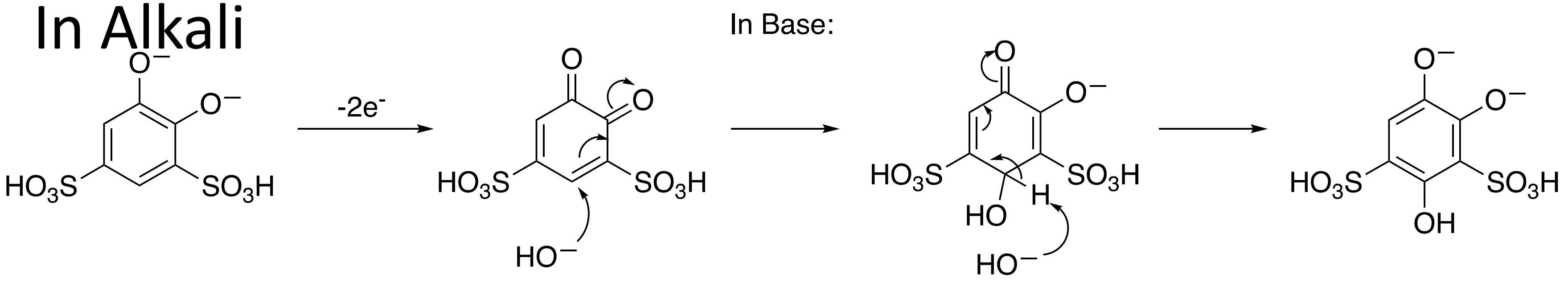
- Occurs more readily on electron-deficient systems



In Acid

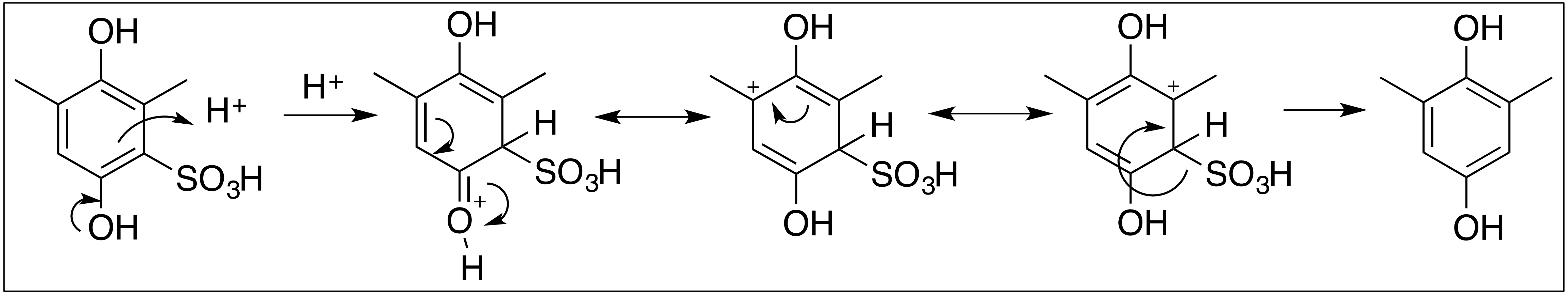


In Alkali



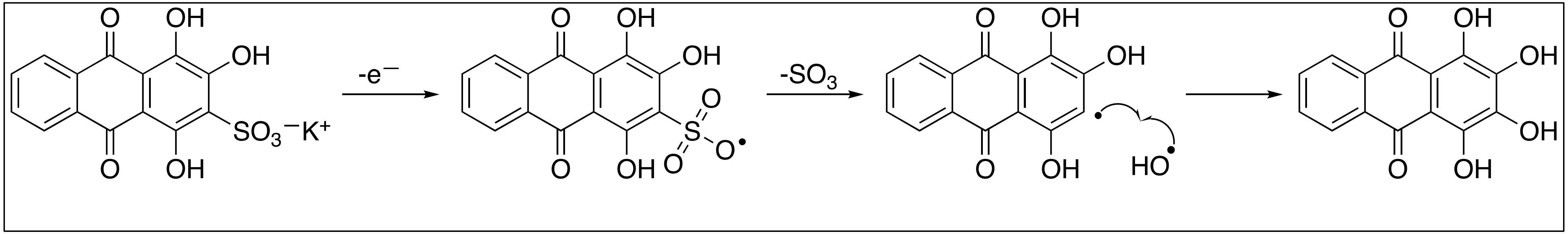
Desulfonation Processes (acid medium)

Proto-desulfonation in Acid: Loss of sulfonic acid group

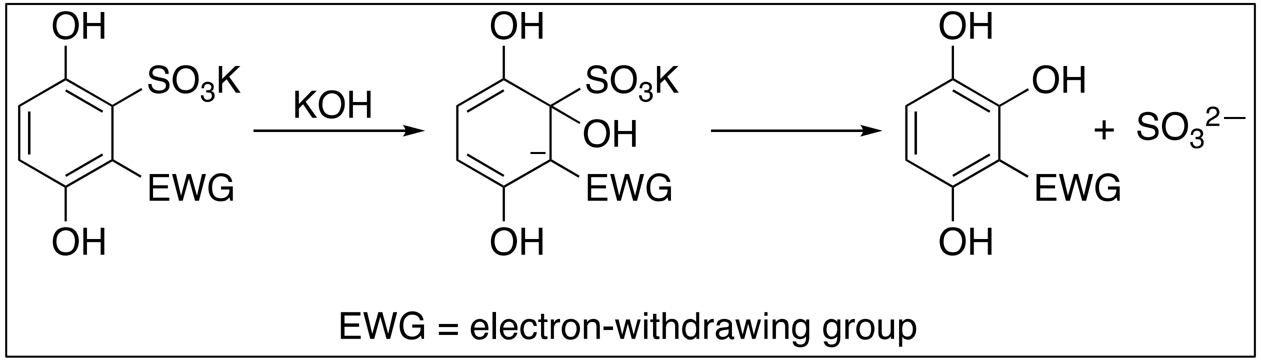


Desulfonation Processes (alkaline medium)

- Oxidative Hydroxy-desulfonation



- Nucleophilic (S_NAR) Hydroxy-desulfonation



Technical Approach

- To reduce the propensity for *Desulfonation* and *Michael Reactions*
  - Examine the effect of substitution by alkyl and phenyl groups on benzoquinone rings
  - Examine these reactivities in bi-functional molecules
- Adding functional groups to increase solubility without increasing reactivity.
- Developing procedures for in-house synthesis of compounds
- Follow the stability changes by NMR and GC-MS to determine effects of long-term cycling
- Electrochemical kinetics testing using RDE and CV on glassy carbon/graphite
- Establishing solubility in charged and discharged state
- Establish decay rates by extended cycling in symmetric cell configuration in flow cells (25 cm^2)

Tasks to Address Challenges

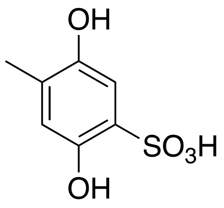
- Task 1. Synthesis, purification and scale-up of materials.
- Task 2. Electrochemical characterization of charge/discharge reversibility and electrode potential.
- Task 3. Characterization of solubility and diffusion coefficient
- Task 4. Crossover rate studies
- Task 5. Passive and active durability studies using flow cell and electrolysis
- Task 6. Reporting, Reviews and Publication

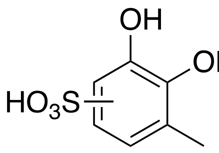
Accomplishments in the past year

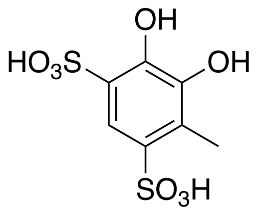
- Several promising benzoquinone derivatives have been synthesized and tested in acid and alkaline media.
- Preliminary results show these molecules possess distinct reactivity and stability based on the substituent groups.
- Verified that anthraquinone-based molecules can be stabilized to make positive side materials and also allow for bifunctional activity to achieve high cell voltage.
- Verified the long-term cycling behavior of stabilized redox materials.

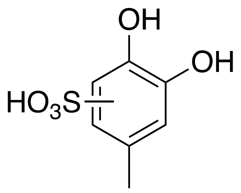
Three Classes of Benzoquinone-derived Positive Side Materials

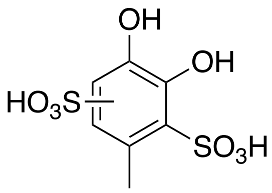
Alkyl-substituted

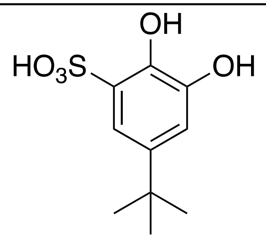

MMS

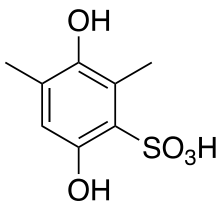

O3MMS

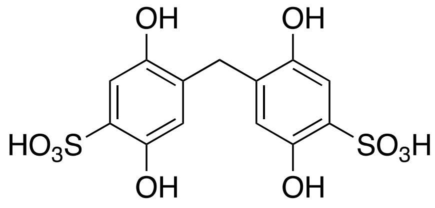

O3MDS


O4MMS

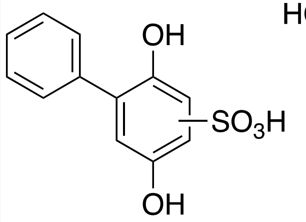

O4MDS

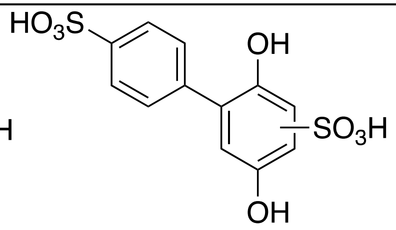

O4TBMS

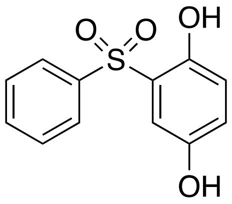

DHDMBS

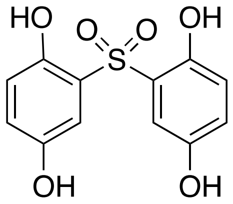

DHQDS

Aryl-substituted

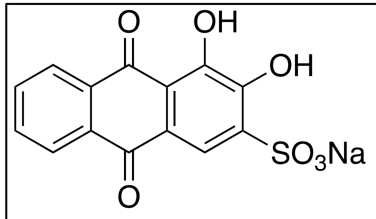

PHQS

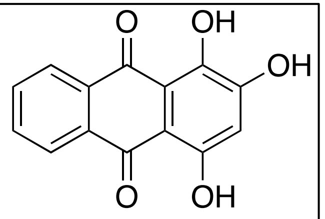

PHQDS


PSHQ

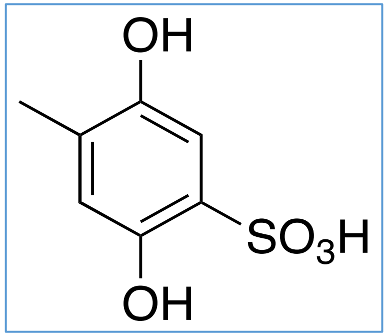

BHQS

Anthraquinone–derived


Alizarin Red

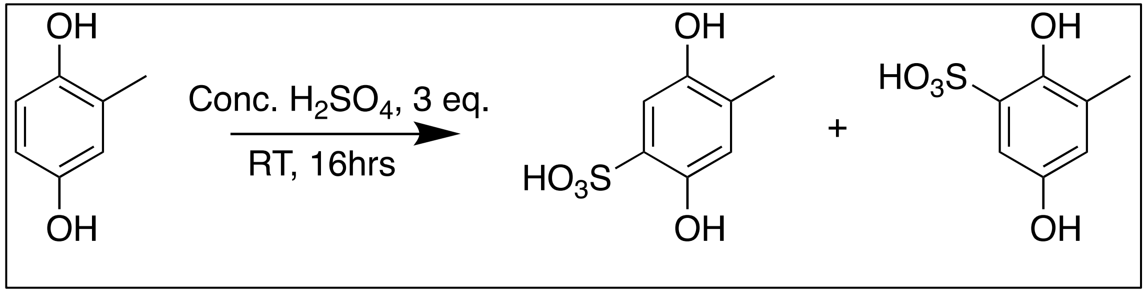

Purpurin

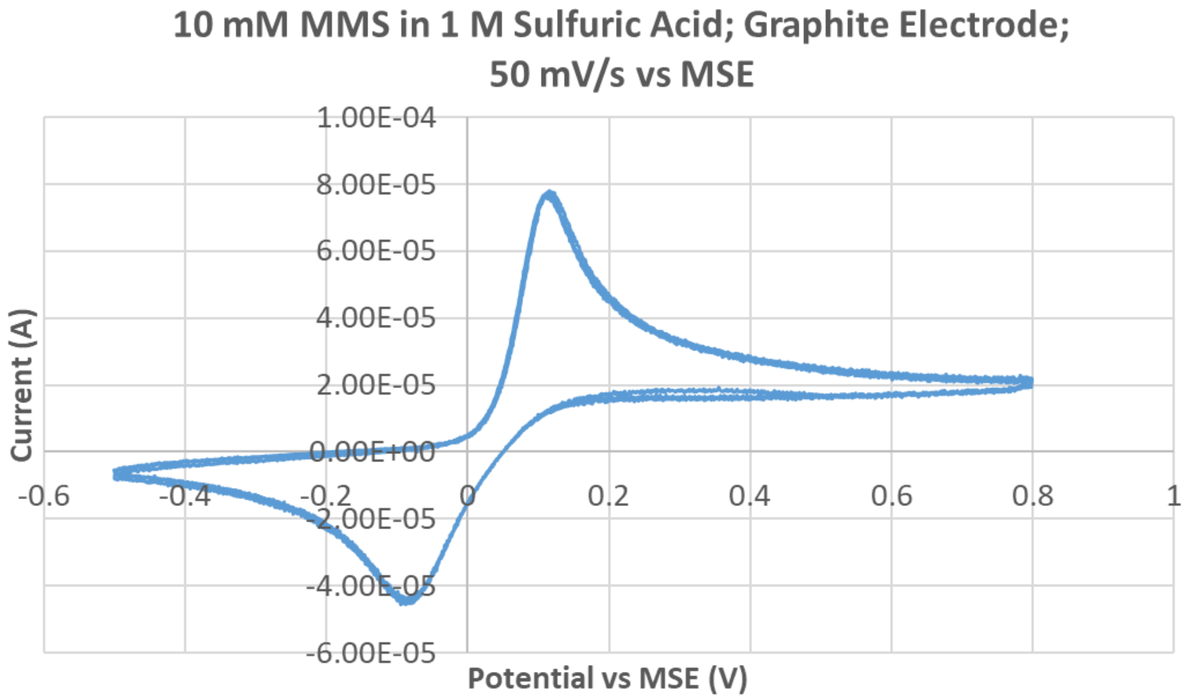
Studies on 6-methyl hydroquinone-3-sulfonic acid (MMS)



MMS

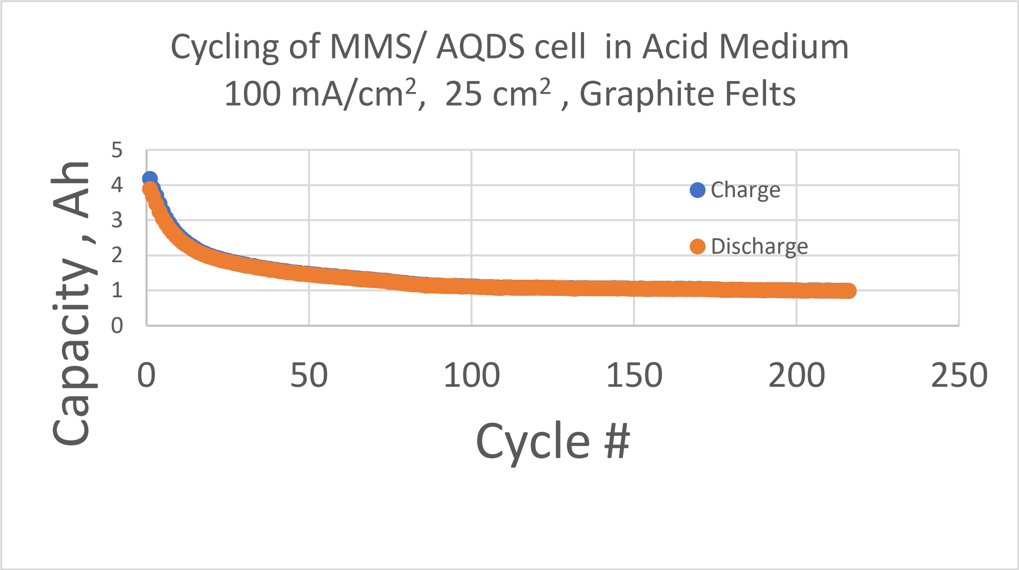
Synthesis



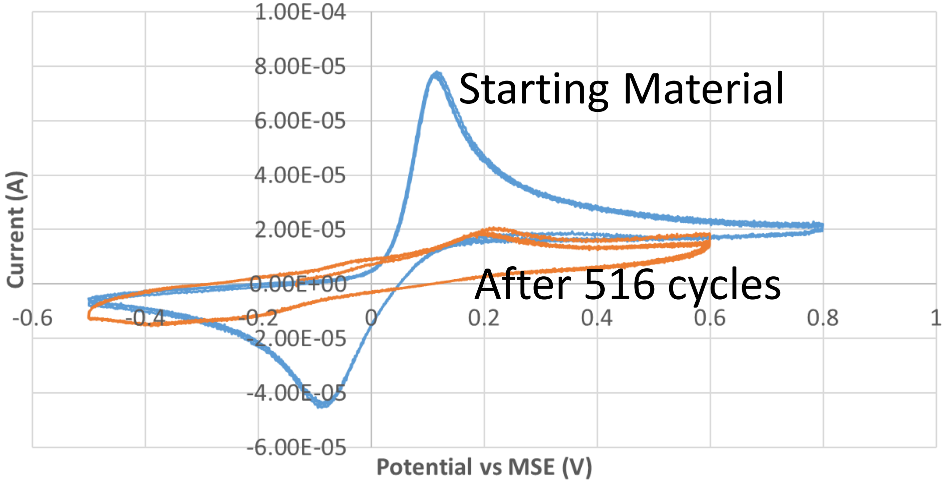


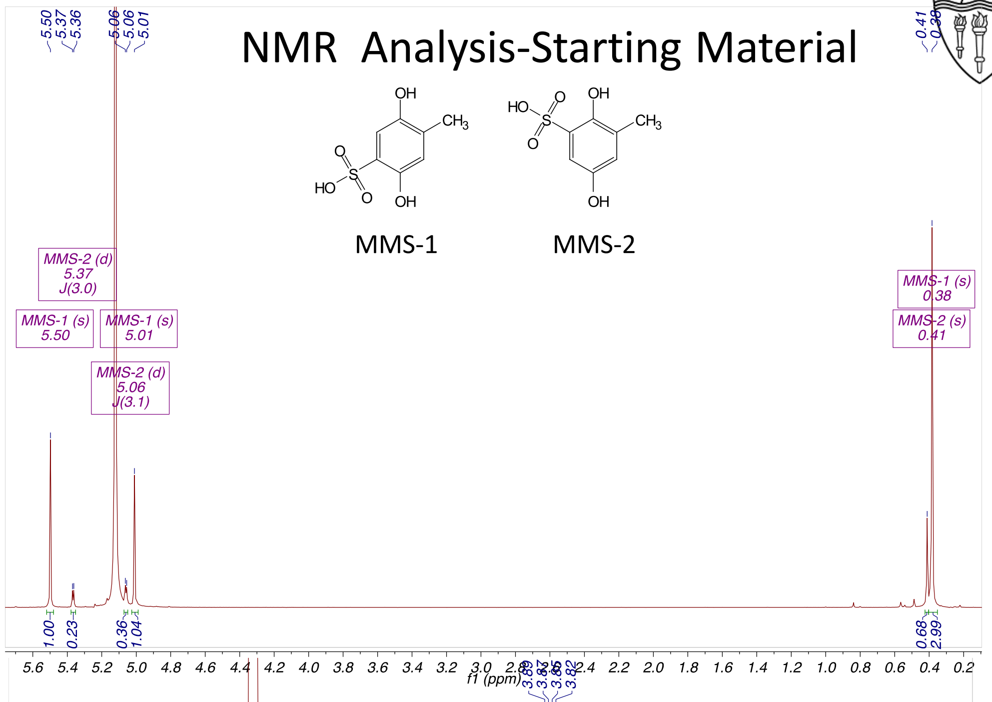
- Cyclic voltammograms suggest excellent reversibility.
- Slow chemical transformations are not captured in a CV.

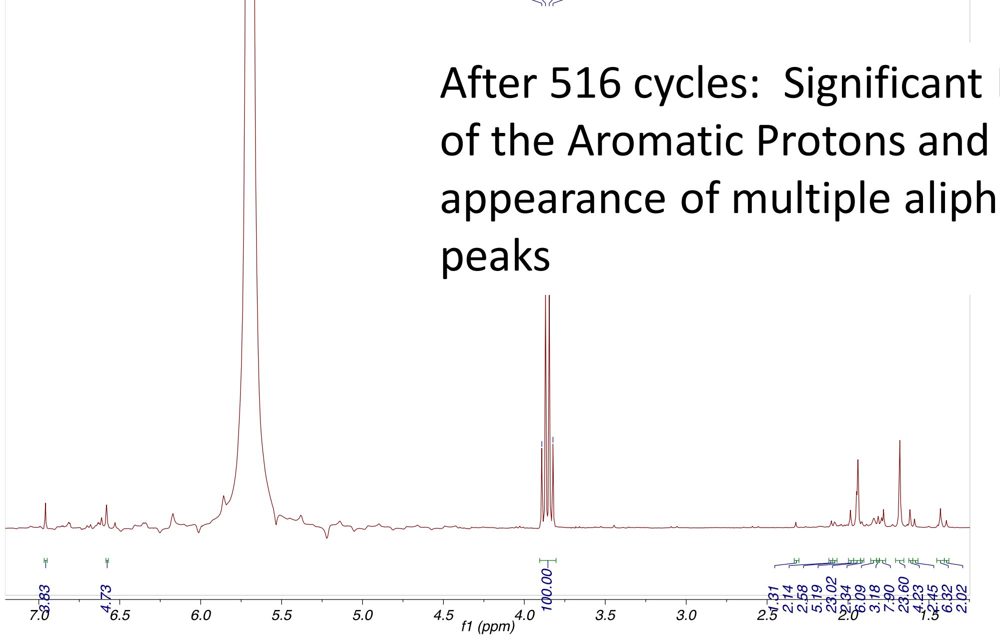
Cycling studies on MMS



CV at 50 mV/s,Graphite Electrode
in 1 M Sulfuric Acid



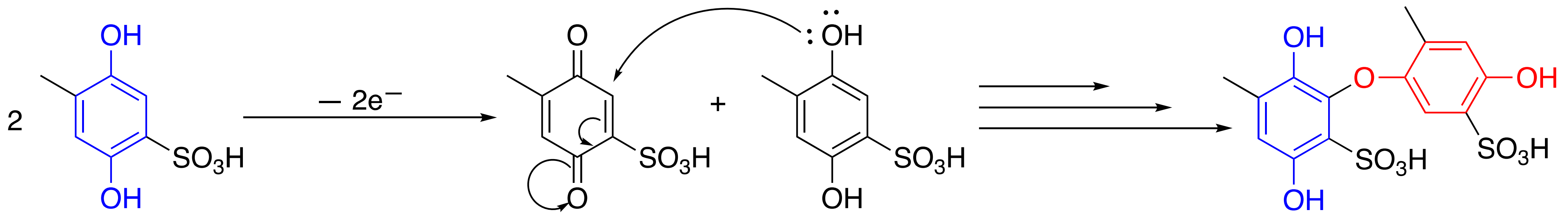




After 516 cycles: Significant Loss of the Aromatic Protons and appearance of multiple aliphatic peaks

Polymerization of MMS

- Shown: dimerization

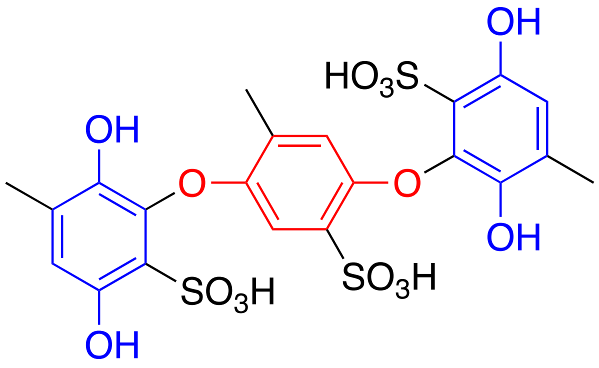


2 equiv of redox-active material

1 equiv quinone + 1 equiv hydroquinone

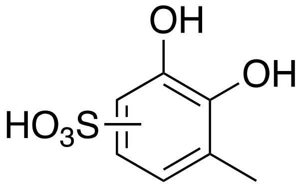
1 equiv redox-active material
(second ring not oxidizable)

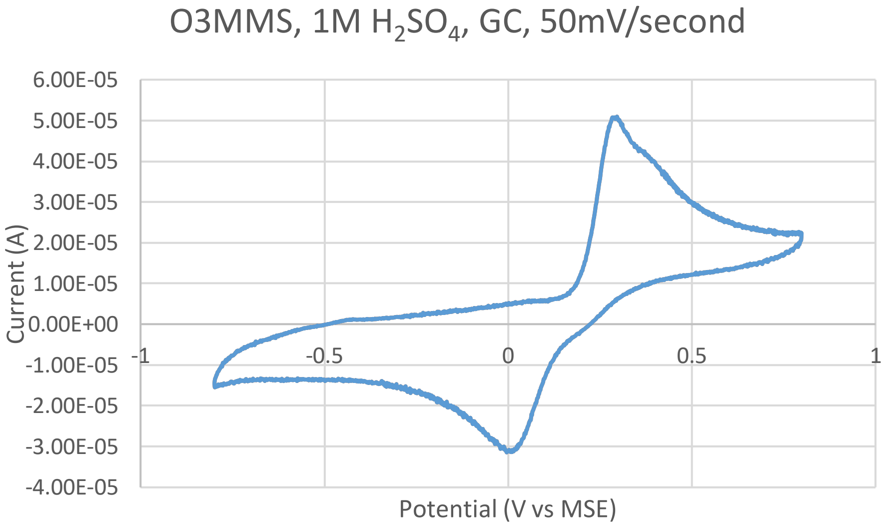
- Process can continue (chain propagation) to form redox active oligomers

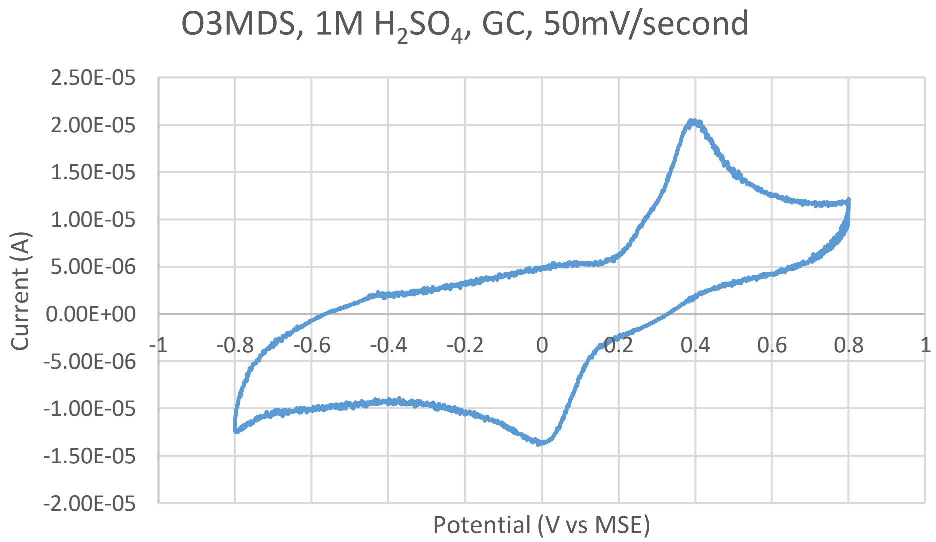


CV Characterization of O3MMS, O4MMS, O3MDS

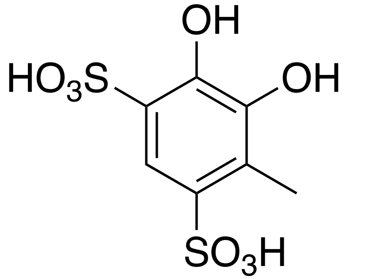
O3MMS

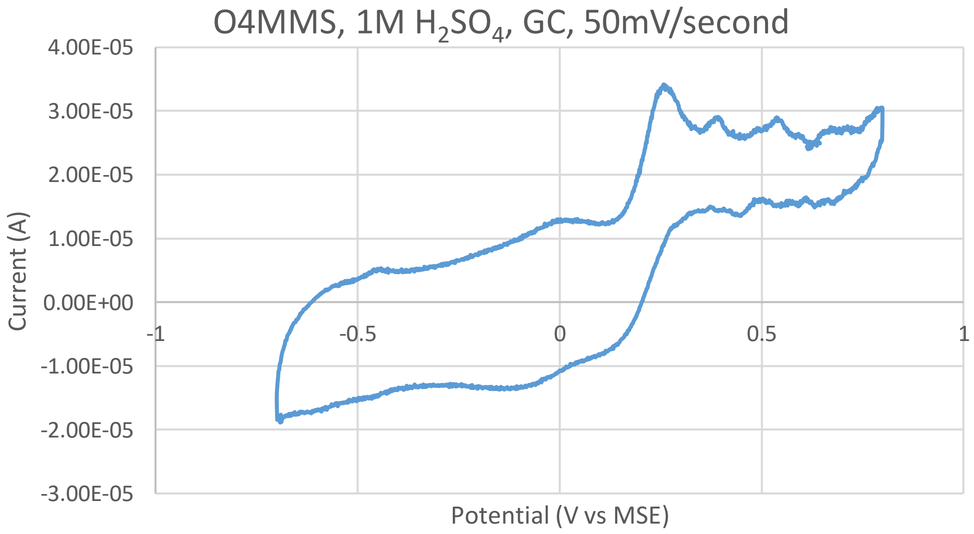




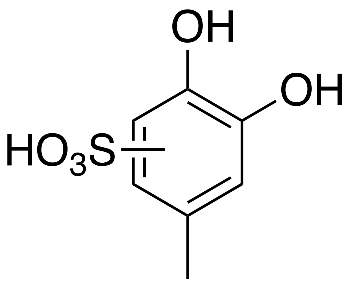


O3MDS



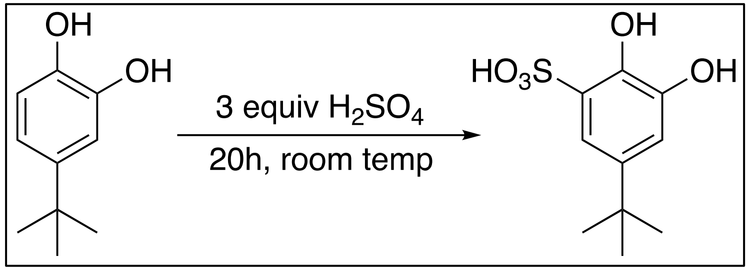


O4MMS

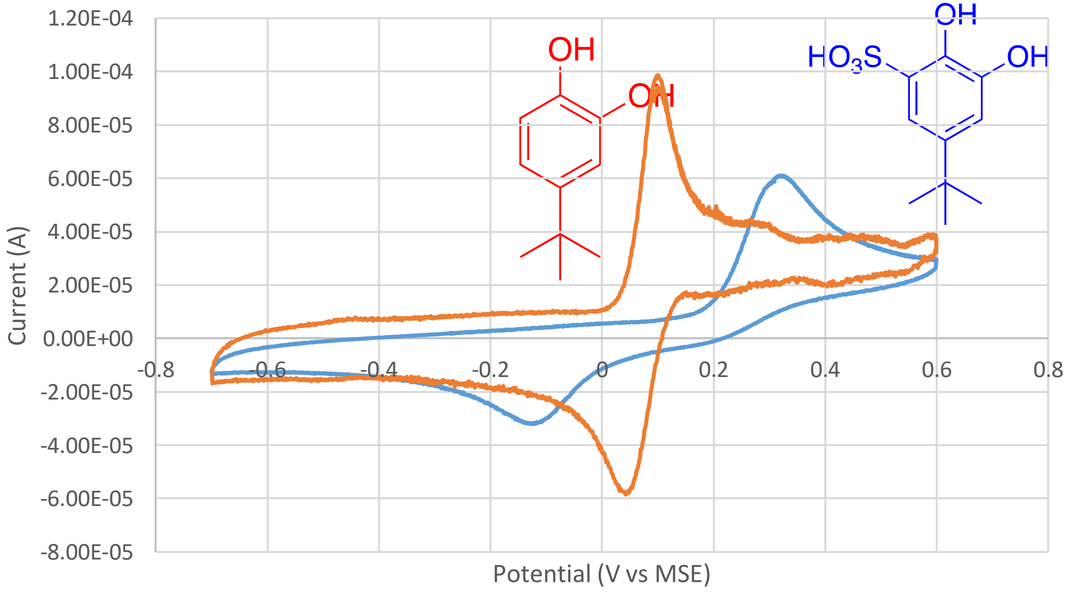


Tertiary-Butyl Substituted Orthobenzoquinone monosulfonic acid (O4TBMS)

Synthesis

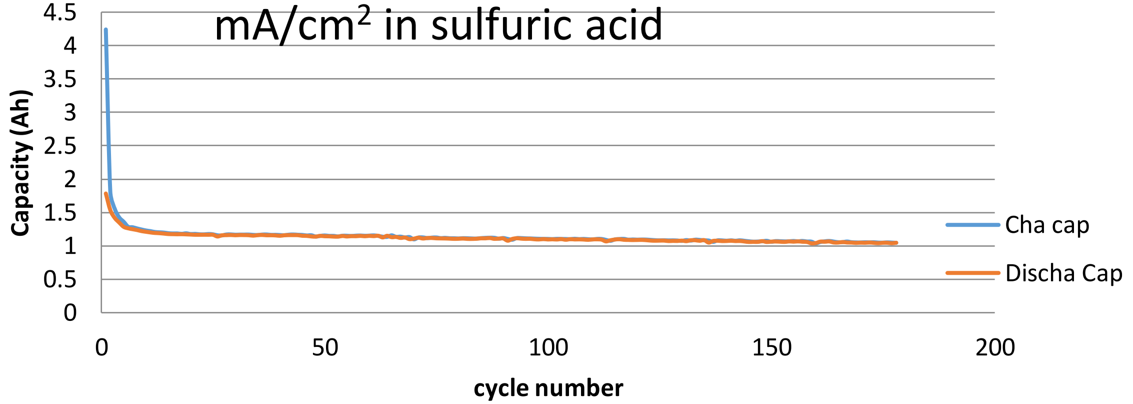


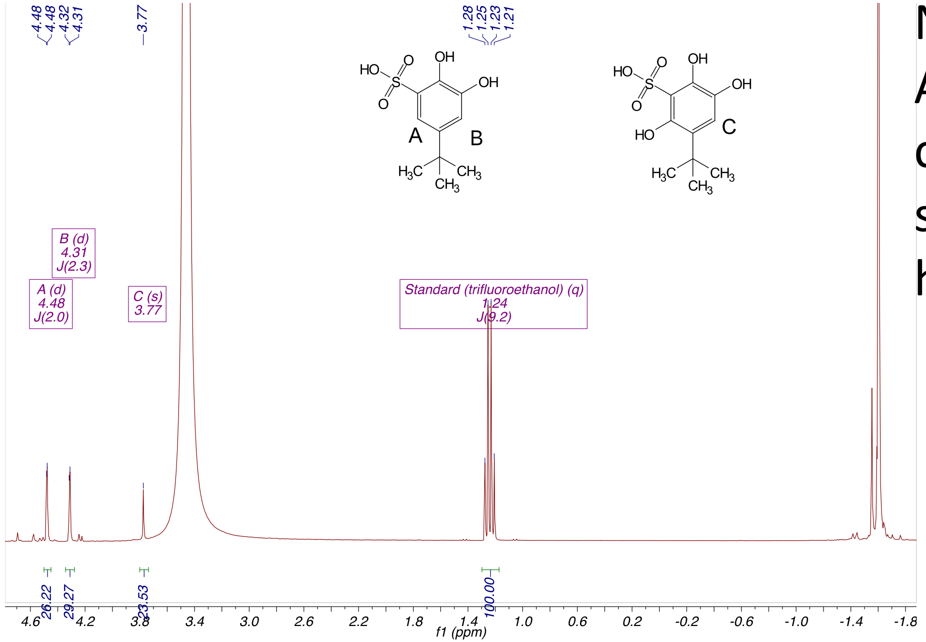
O4TBMS, 1M H_2SO_4, GC, 50mV/second



Potential shift to positive values upon sulfonation

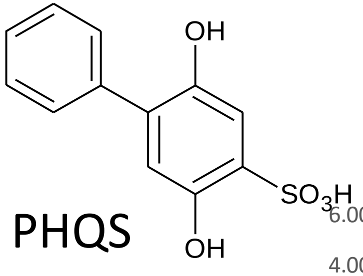
1M O4TBMS/ 1M AQDS cell cycled at 100 mA/cm^2 in sulfuric acid



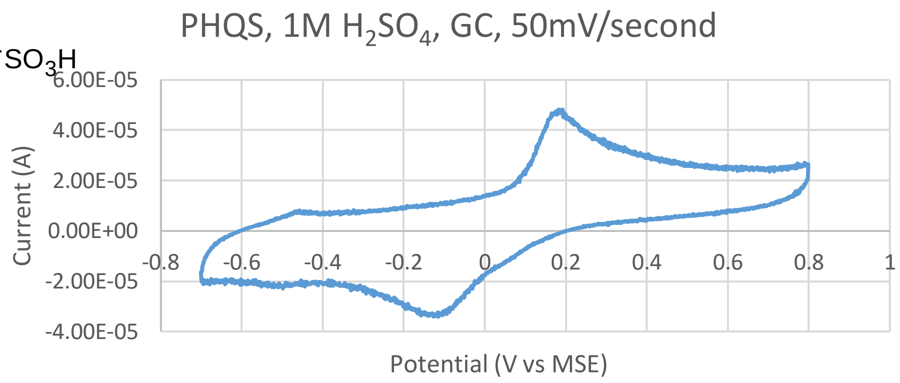


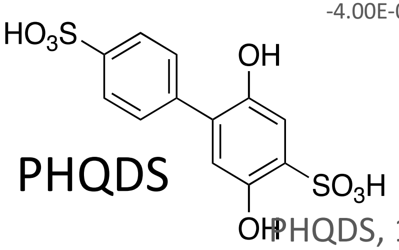
NMR Analysis confirms fast single step hydroxylation

Aryl-Substituted benzoquinones PHQS, PHQDS, Aryl sulfones

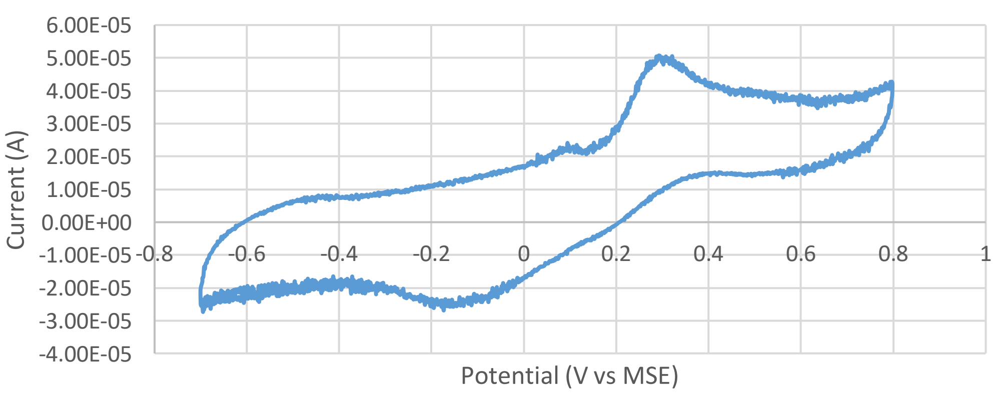


PHQS

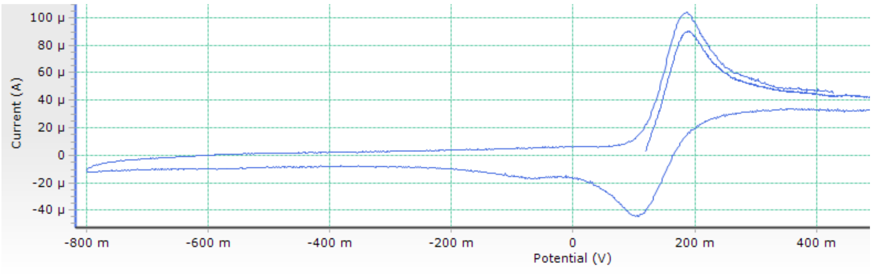


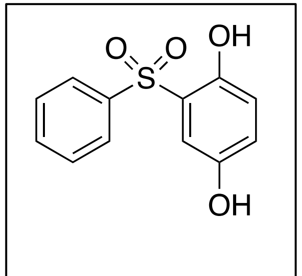


PHQDS

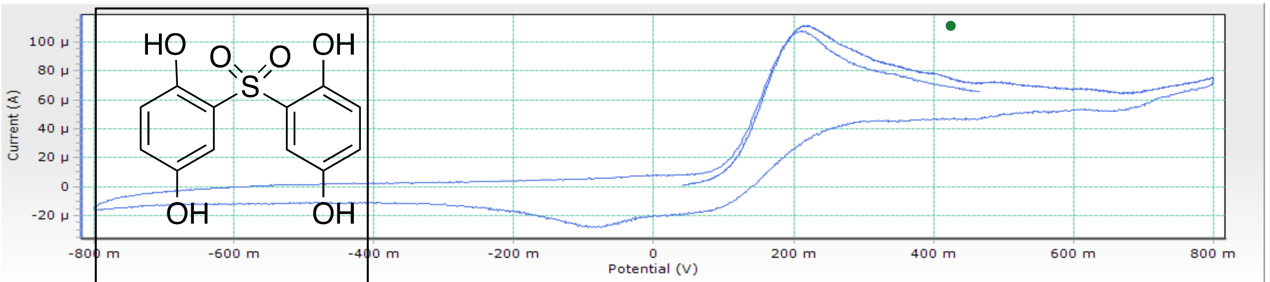


Aryl sulfones



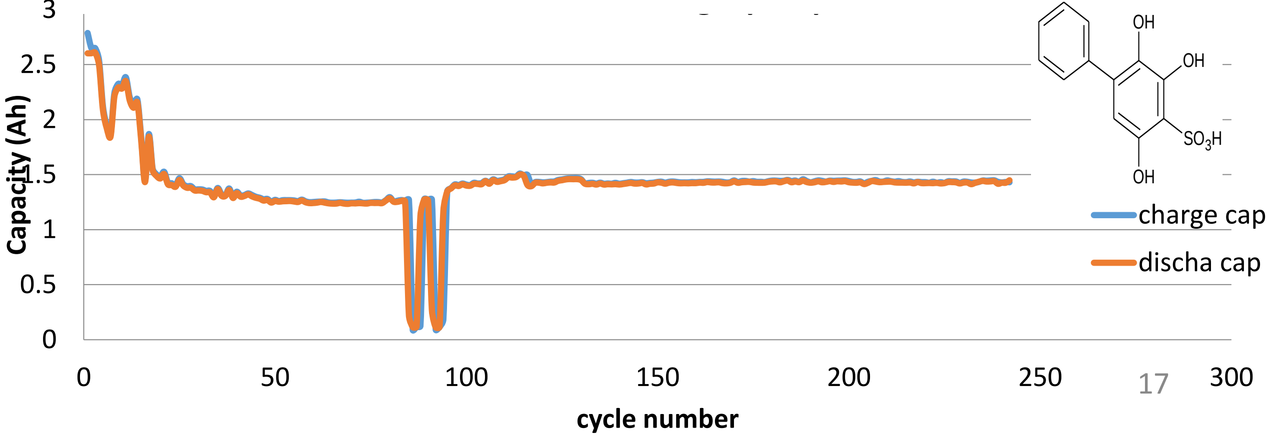


PSHQ

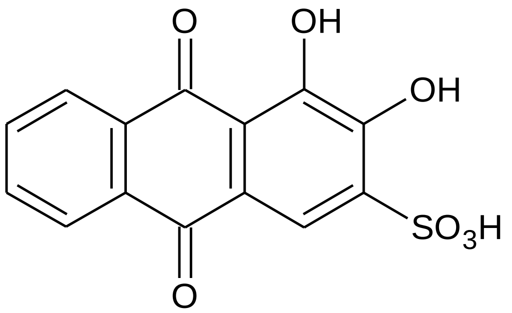


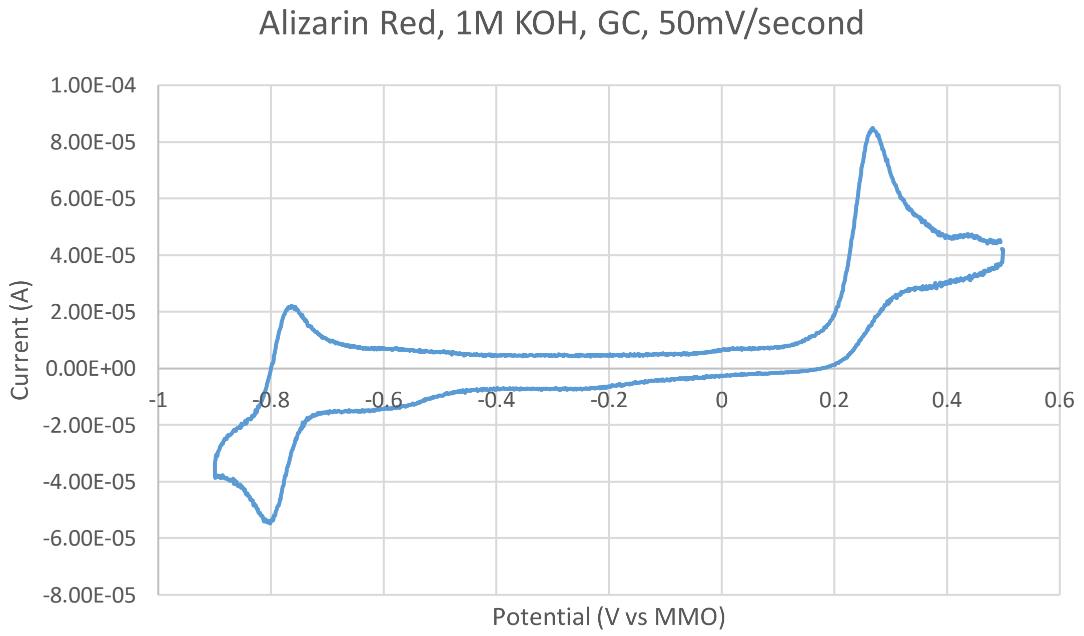
BHQS

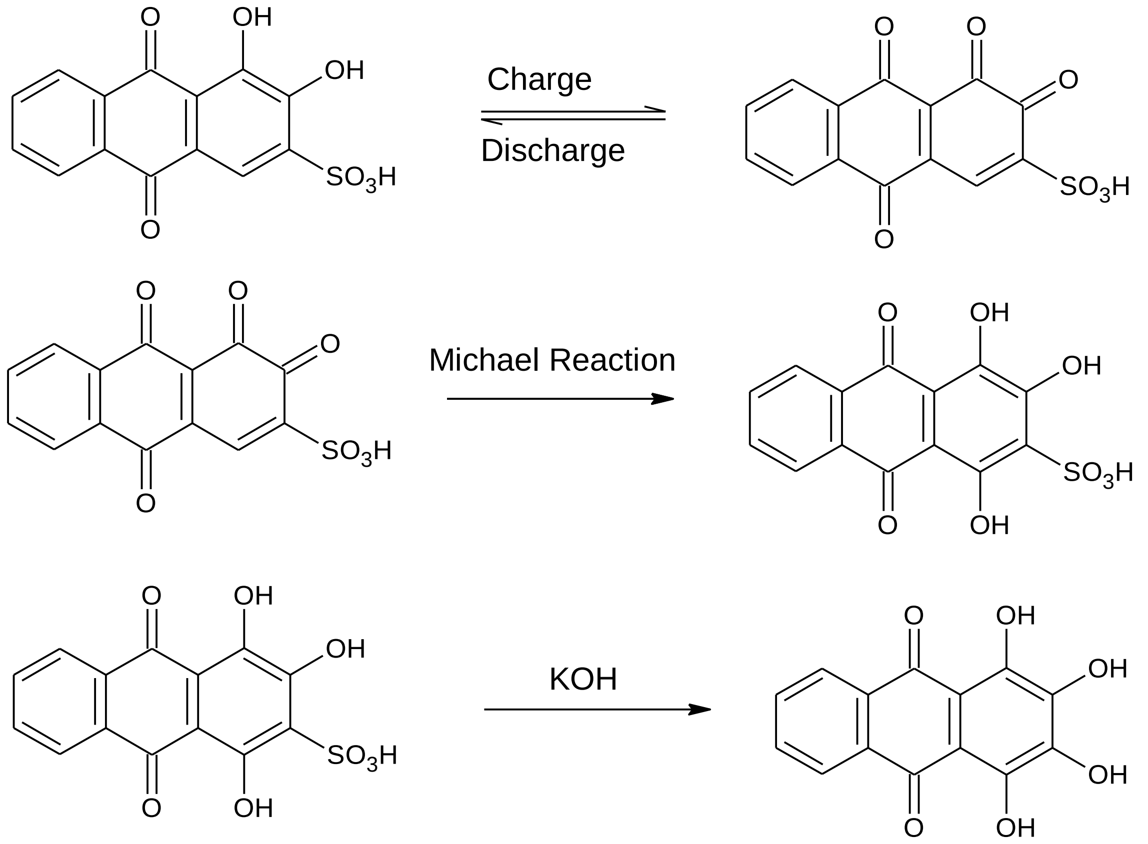
Cycling of PHQS /AQDS cell in 1M sulfuric acid at 100 mA/cm^2



Bifunctional Anthraquinone –Derived Molecules- Alizarin Red in Alkaline Media

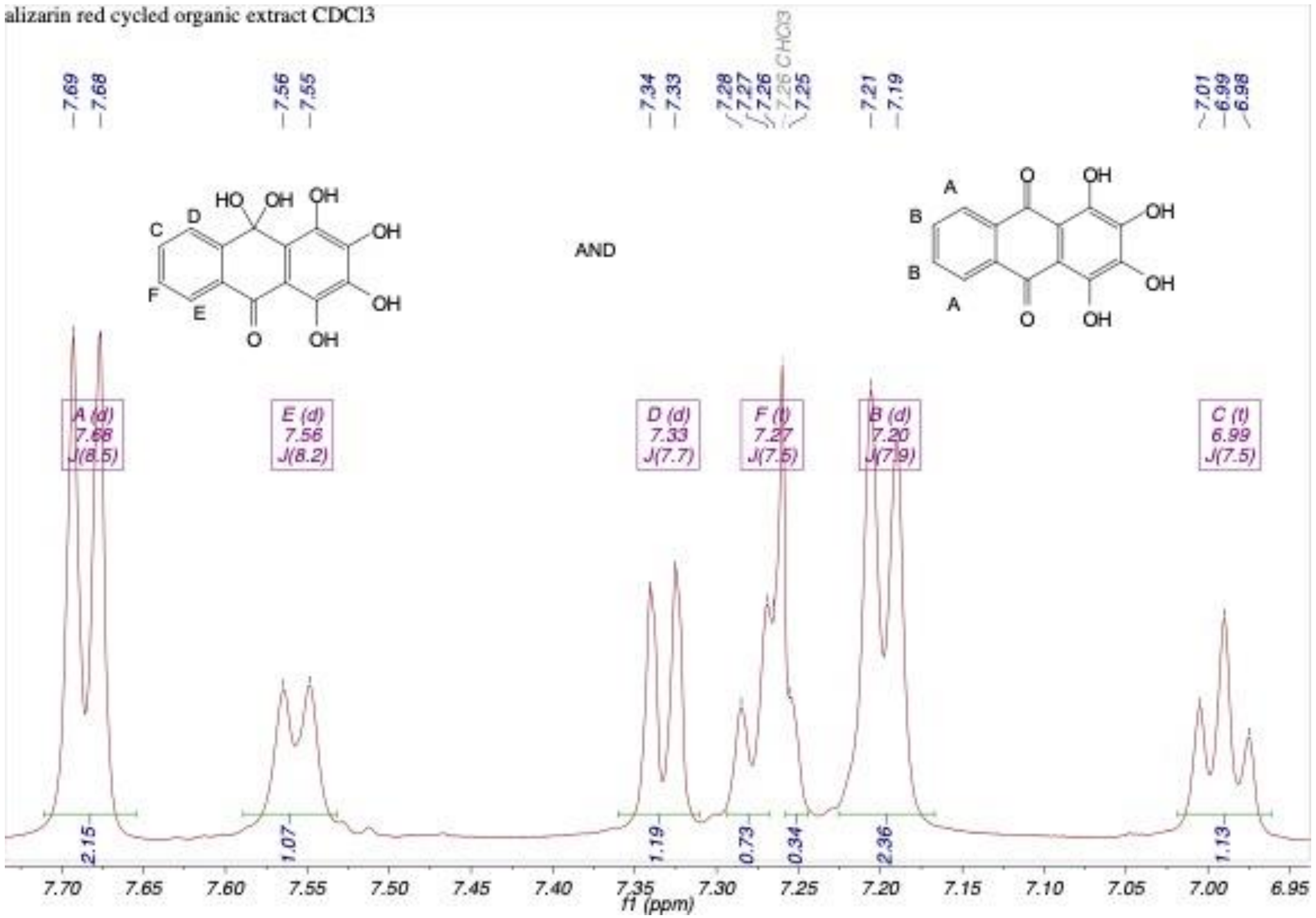






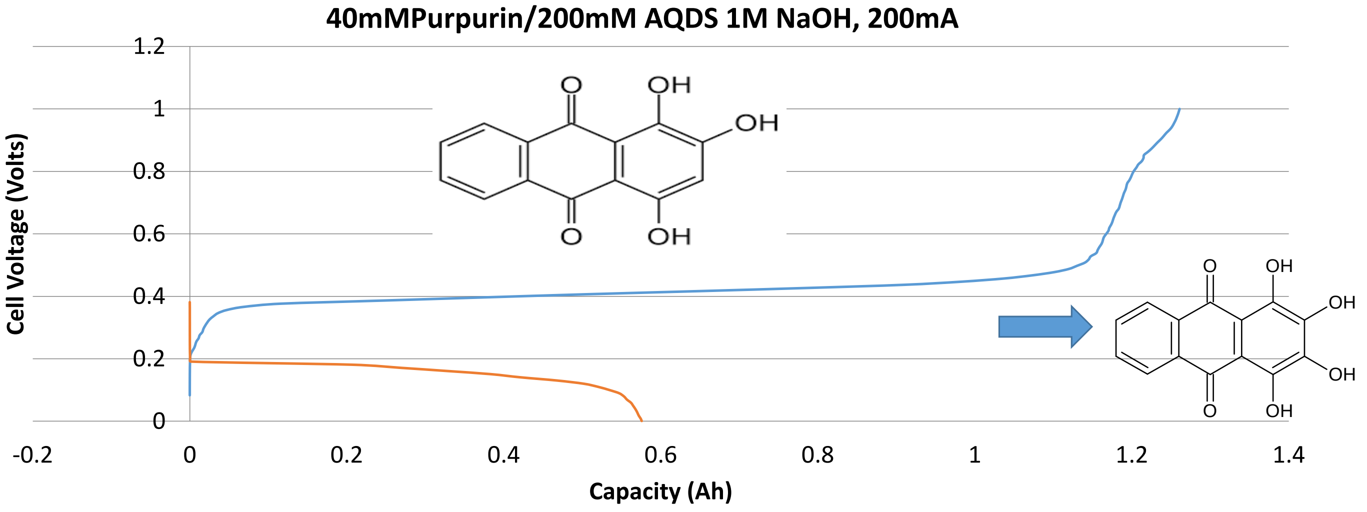
Hydroxydesulfonation of Alizarin Red

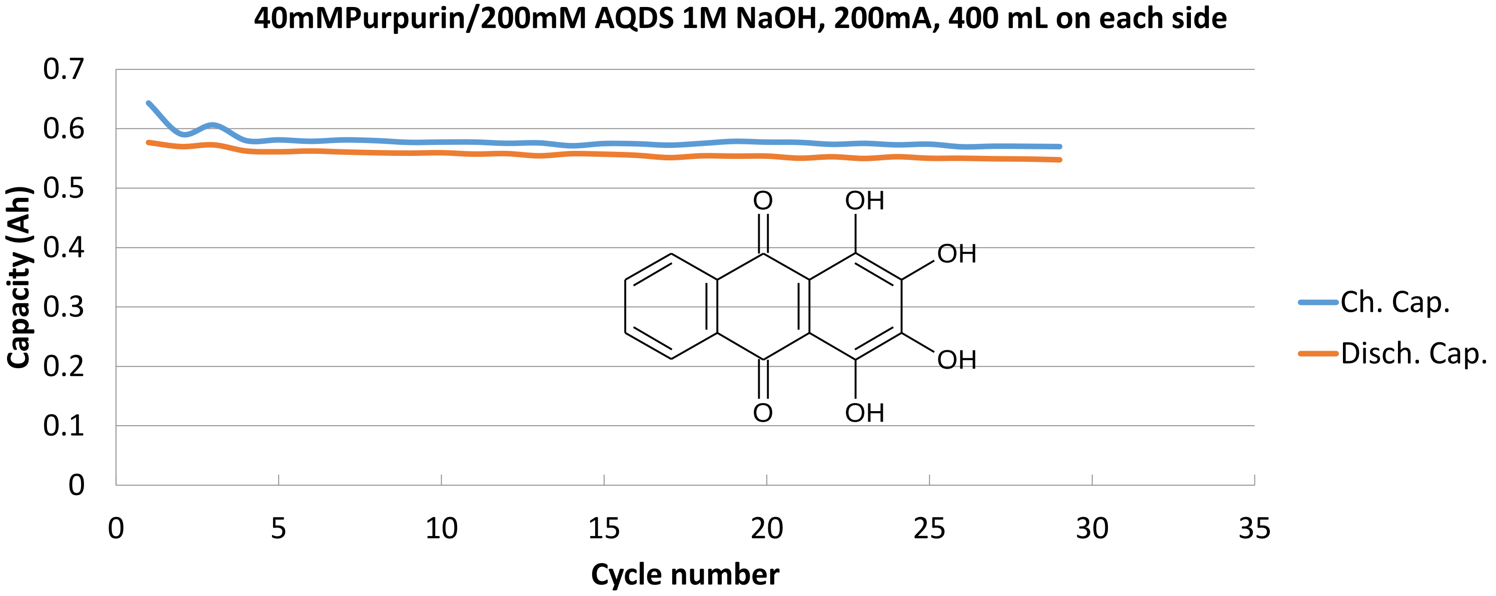
NMR Analysis of cycled Alizarin Red



Confirms the formation of the tetrahydroxylated product

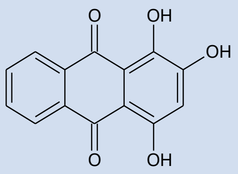
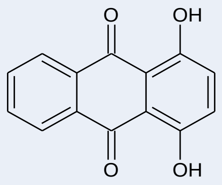
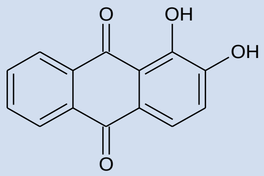
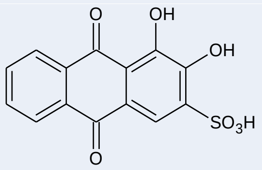
Purpurin-a viable pathway to using anthraquinone derivatives

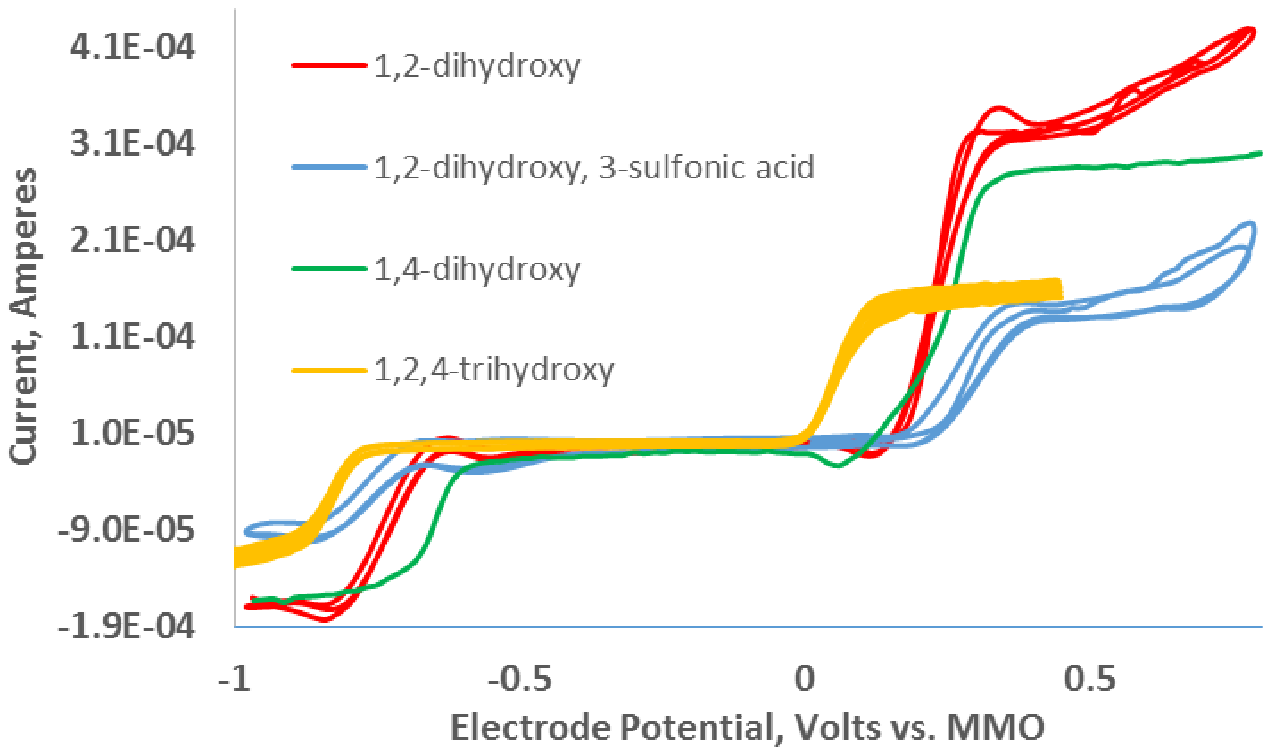




Hydroxylated Purpurin can be cycled in alkali without noticeable degradation

Other Promising Bifunctional Molecules Studied

Compound	Structure	$E_{1/2}$ (Volts) vs MMO	Bi-functional Mate Potential
1,2,4-trihydroxy anthraquinone		-0.84 V	Yes, 840 mV differe
1,4-dihydroxy anthraquinone		-0.63 V	Yes, 880 mV differe
1,2-dihydroxy anthraquinone		-0.73 V	Yes, 1 V difference
1,2-dihydroxy, 3-sulfonic acid anthraquinone		-0.75 V	Yes, 930 mV differe



Potential to increase cell voltage by substitution

Next Steps

- Increase the solubility of stable redox molecules to ensure high concentrations.
- Develop methods of sulfonation for the non-participating ring.
- Complete the characterization in alkaline media
- Down-select molecules for full-cell testing
- Pursue further molecular designs to avoid oligomer formation.
- Explore the bifunctional nature of stabilized redox molecules in full cell.

Acknowledgements

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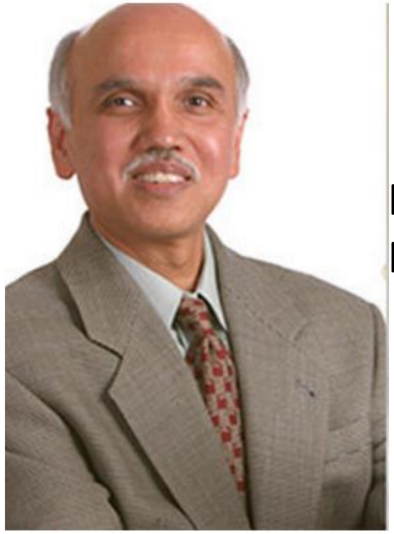

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